

Determination of Unsaturation by Microhydrogenation

Method and Apparatus

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An apparatus and method for quantitative microhydrogenation are described. The simple design of the apparatus is made possible by use of magnetic stirring to agitate the reaction mixture. Data are presented to indicate the precision and accuracy of the method.

QUANTITATIVE hydrogenation as a means of measuring unsaturation has several advantages over the halogenation methods commonly used. This method is not subject to the errors resulting from the presence of two or more conjugated double bonds or from complex molecular structure. Except for choosing the correct catalyst for determining aromatic or aliphatic unsaturation, conditions for hydrogenation do not have to be empirically adjusted to the material being analyzed, as do those for halogenation. In general, hydrogenation is more reliable, for it eliminates the necessity of previous knowledge of the molecular structure.

Another important advantage is that a high catalyst-to-sample ratio can be used. This aids in obtaining complete hydrogenation and in overcoming the effects of poisoning the catalyst by small amounts of sample impurities. Halogenation micromethods are seldom used because of the many inherent errors.

Several authors have described hydrogenation microapparatus that have given reliable results. Among them are Johns and Seiferle (1), whose relatively simple apparatus was mounted on a plywood board and shaken as a single unit to agitate the reaction mixture. The apparatus of Prater and Haagen-Smit (3) was also mounted rigidly and rocked by an eccentric driven by a motor. It had two completely symmetrical systems, which were connected; one served as the reaction system and the other as the compensator. When no temperature compensation was necessary, two determinations could be run simultaneously.

The apparatus described here is more simply constructed and much more easily assembled than the two just mentioned, for a stationary reaction vessel is used and agitation is produced by magnetic stirring. This type of agitation for hydrogenation was first described by Weygand and Werner (4) and more recently by Zaugg and Lauer (5), whose semimicroapparatus was designed for both Grignard and hydrogenation determinations. Although Weygand and Werner's apparatus is the simplest yet described, the manometer-buret assembly with rack and pinion device for

leveling bulb adjustment described here makes possible more accurate volume measurements. This part of the apparatus is adapted from the Soltys' active hydrogen apparatus sold by Arthur H. Thomas Company. The ball joint connection gives the apparatus greater flexibility, and the detachable reaction vessel with standard-taper joint is easily accessible for cleaning.

APPARATUS

Figure 1 shows the apparatus and hydrogen purification train.

The purification train consists of a standard micro electric combustion furnace, *A*, heated to approximately 750° C. so that the platinum star contact catalysts, *C*, in the 8-mm. inside diameter quartz combustion tube, *B*, will effectively remove the oxygen from the hydrogen gas. The water so formed is absorbed by indicating Drierite in the inner tube of the Prater (2) semimicro absorption tube, *D*. If the hydrogen gas is wet, it is advisa-

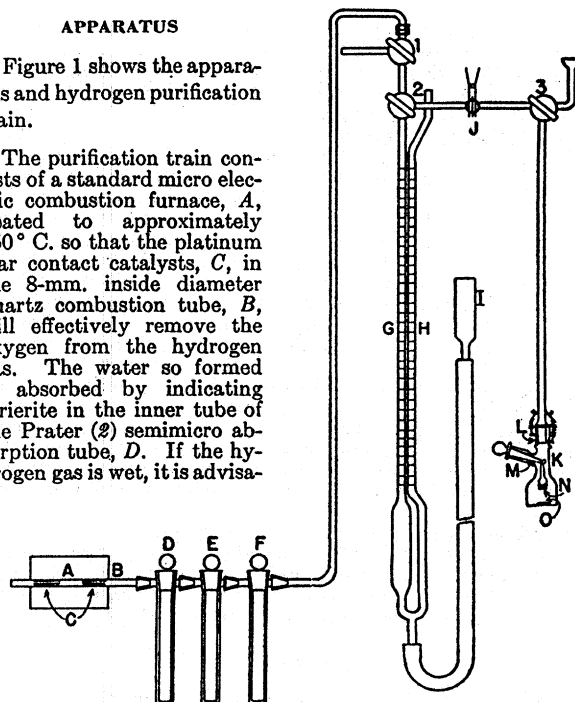


Figure 1. Hydrogenation Microapparatus

ble to place a drying tube before the combustion tube to remove the moisture and thus prolong the life of the absorbent in *D*.

Tubes *E* and *F* are used to saturate hydrogen with the solvent to be used in the reaction vessel. One inch (2.5 cm.) of the solvent is placed in *E*, and the inner tube of *F* is filled with glass wool to prevent mechanical carry-over of the solvent.

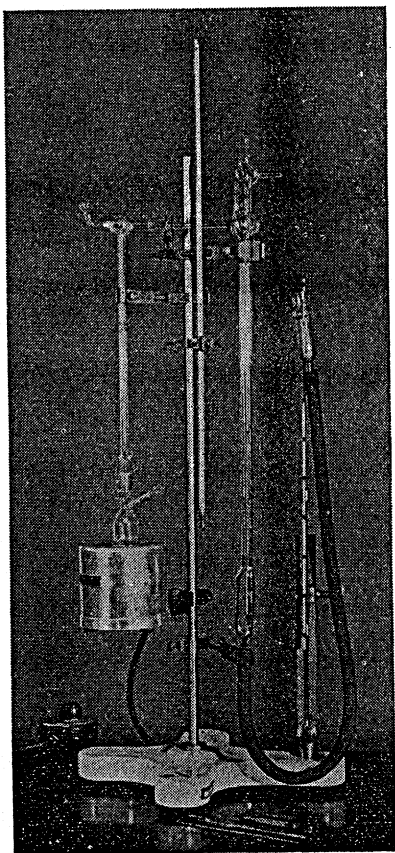


Figure 2. Hydrogenation Assembly and Accessories

All the $7/16$ standard-taper ground joints in the hydrogen train are sealed with de Khotinsky cement. The purification train is attached to stopcock 1 of the apparatus by a glass tubing with a Tygon tubing connector. Buret *G* and manometer *H* have parallel and coinciding graduations, with 0.02-ml. intervals from 0 to 7 ml. Mercury is leveled in *G* and *H* by raising or lowering leveling bulb *I* with a rack and pinion device shown in Figure 2. The reaction unit is connected to the buret by the 12/2 ball joint, *J*, held in place by a suitable clamp. The 20-ml. reaction flask, *K*, is connected by a 14/20 ground-glass joint, *L*, and held in place by two steel springs. Side arm and stopper *M* are made from 10/12 ground joints. The stopper, which extends into the neck of the flask, has a groove near the tip and perpendicular to its long axis. Sample cup *N* is hung on the stopper and dropped by turning *M*. *N* is made by drilling an aluminum rod about 6 mm. in diameter and 8 mm. long so that its volume is about 0.1 ml. The Nichrome wire handle is attached through two holes drilled on opposite sides of the cup. The stirring bar, *O*, is made by sealing fine iron filings in a glass tube about 3 mm. in outside diameter and about 15 mm. long. The cup attached to stopcock 3 facilitates cleaning the tube leading to the reaction vessel. Stopper *M* and joint *L* are greased carefully before each analysis, and the stopcocks and ball joint are lubricated frequently to prevent loss of hydrogen.

Figure 2 shows the apparatus, including the magnetic stirrer assembly, support stand with rack and pinion, and other necessary equipment. The thermometer (range, 0° to 100° C.; graduated in 0.1°) is hung between the buret and reaction vessel. All temperature readings are made to the nearest 0.1°.

CATALYST

One gram of palladium chloride is dissolved in 25 ml. of distilled water and added to a 50-ml. water suspension of 6 grams of

activated carbon. This mixture is transferred to a pressure bottle and hydrogenated under 35 pounds' pressure (2.46 kg. per sq. cm.) in a Burgess-Parr apparatus for 0.5 hour. The suspension is transferred to a Büchner funnel, the solvent is drawn off, and the catalyst is washed with water until the washings are free of hydrochloric acid. Volatile and flammable wash liquids should be avoided because the palladium catalyst may ignite the liquid. The catalyst is dried at room temperature in a vacuum oven for 16 to 20 hours, then stored in a desiccator over phosphorus pentoxide.

METHOD

Operation of the hydrogen purification train is started by causing hydrogen to flow from a pressure tank through the train and through stopcock 1, where it is vented to the atmosphere. The hydrogen pressure is adjusted to approximately 1 pound by the tank pressure-reducing valve, and the flow is adjusted to 25 to 35 ml. per minute. Furnace *A* is turned on, and after it has reached operating temperature, the hydrogen flow is stopped by turning stopcock 1. The gas in the train is under the same positive pressure as that in the reducing valve.

Four milliliters of redistilled acetic acid, about 20 mg. of catalyst, and the stirring rod are placed in the reaction flask. The aluminum cup containing a weighed sample equivalent to 3 to 5 ml. of hydrogen is suspended from the stopper in the reaction vessel by grasping the wire handle with tweezers and lowering the cup into the flask so that the handle rests in the groove of stopper *M*. Reaction flask *K* is attached to the apparatus and held in place with the springs. The burette is filled with mercury to stopcock 2, which is then turned to close the burette.

Stopper *M* is loosened, and the reaction unit is swept with hydrogen by turning stopcocks 1, 2, and 3 to allow the hydrogen to flow through the unit at a rate of 25 to 35 ml. per minute. After 15 minutes, *M* is seated firmly, stopcock 2 is turned to connect the buret to the purification train, and the buret is filled with hydrogen. Stopcock 1 is given a $1/8$ turn to close all openings, and stopcock 2 is turned so that the buret is connected with the reaction unit. The hydrogen in the buret is placed under positive pressure by raising the leveling bulb, and the excess pressure is released by momentarily opening stopcock 3. The acetic acid and catalyst are stirred for 5 minutes after diminution of the gas volume ceases. The magnetic stirrer is moved from under the reaction flask, and the apparatus is allowed to equilibrate for 15 minutes before the volume, temperature, and pressure are read and recorded.

The cup containing the sample is dropped into the flask by turning stopper *M*, and the reaction mixture is stirred vigorously for 15 minutes after hydrogen uptake has ceased (about 30 minutes), as indicated by the manometer. Throughout the analysis, the mercury levels in the buret and manometer should not differ by more than 1 cm. The magnetic stirrer is removed, and after the apparatus is equilibrated for 15 minutes, the final volume, temperature, and pressure are recorded.

CALCULATION

- V_i = buret reading before reaction of sample
- T_i = temperature before reaction of sample
- P_i = pressure before reaction of sample
- V_f = buret reading after reaction of sample
- T_f = temperature after reaction of sample
- P_f = pressure after reaction of sample
- V_t = total gas volume of the reaction unit plus the volume of the buret above the zero mark
- $P_{s,i}$ = vapor pressure of solvent at temperatures T_i
- $P_{s,f}$ = vapor pressure of solvent at temperatures T_f
- $V_i + V_t \times 273/T_i \times (P_i - P_{s,i})/760 = V_i' = \text{volume of H}_2 \text{ at S.T.P. before reaction}$
- $V_f + V_t \times 273/T_f \times (P_f - P_{s,f})/760 = V_f' = \text{volume of H}_2 \text{ at S.T.P. after reaction}$
- $\text{Wt. of sample}/(V_i' - V_f') \times 22,400 = \text{hydrogen number} = \text{weight of sample that will react with 1 mole of hydrogen}$

RESULTS

This method with palladium catalyst has been used successfully for determining the unsaturation of a number of fatty acids and their esters. Table I shows the hydrogen numbers obtained for some of these materials. The differences between the calculated and found values are less than 1 for all samples except methyl oleate. For this sample, hydrogenation gave an average value (298.7) midway between the calculated value (296.5) and that obtained by halogenation (300.7). The precision of the method is

Table I. Hydrogen Numbers for Some Unsaturated Acids and Esters

Sample	Hydrogen Number		
	Found	Average	Calculated
Maleic acid	115.0	115.9 ^a	116.1
	118.5		
	118.9		
	115.7		
	115.8		
	115.9		
	116.7		
	115.5		
	115.1		
	115.4		
Methyl oleate	299.9	298.7	296.5
	297.4		
Methyl linoleate	147.2	146.9	147.2
	147.6		
	146.0		
9,11-Linoleic acid	140.4	140.8	140.2
	141.2		
10,12-Linoleic acid	140.4	140.0	140.2
	139.5		
Methyl linoleate (alkali isomerized)	146.4	146.7	147.2
	147.0		
	146.6		
10-Hendecenamide	184.2	183.9	183.3
	183.6		

^a Standard deviation = 0.6.

shown by the standard deviation of 0.6 for the ten values for maleic acid. The accuracy of the method is indicated by the close agreement between the calculated and found values in Table I.

The confidence limits for the mean (115.9 ± 0.5) calculated from the maleic acid analyses brackets the theoretical value and shows that there is no significant inherent error in the method.

In general, the values are 0.2 to 0.5% below those calculated, which means that slightly more than the theoretical amount of hydrogen is consumed during the reaction. This indicates that there is a slight loss of hydrogen by diffusion during the analysis. Further evidence is that the hydrogen volume slowly but continuously diminishes if the apparatus is allowed to stand for several hours. After more data are obtained, it may be possible to correct for this apparent loss by subtracting a blank from the volume of hydrogen used, but probably this will not be greater than 0.01 ml.

The apparatus has been used only in a room in which the temperature is kept under close control. If such a room is not available, it would be advisable to house the apparatus in a cabinet, in which a relatively uniform temperature can be maintained.

LITERATURE CITED

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